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DIALOG(R) File 342: Derwent Patents Citation Indx
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04195947 WPI Acc No: 00-657676/64
Cosmetic composition comprising polymers having original star structure,
for use in preparations for maintaining or fixing hairstyle, or for
treatment of hair
Patent Assignee: (OREA ) L'OREAL SA
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Patent Family:
                                 Examiner Field of Search
 Patent No Kind Date
 EP 1043346 A1 001011 (BASIC)
 CA 2304391
               A1 001006
 DE 60001513 E 030410
 EP 1043346 B1 030305 C08F-293//00
 FR 2791990
               A1 001013
               B2 030304 None
 JP 3383261
 JP 2000319328 A 001121
Derwent Week (Basic): 0064
Priority Data: FR 994258 (990406)
Applications: FR 994258 (990406); DE 601513 (000309); EP 2000400651 (
   000309); CA 2304391 (000406); JP 2000105437 (000406)
Designated States
   (Regional): AL; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LI;
    LT; LU; LV; MC; MK; NL; PT; RO; SE; SI
Derwent Class: A13; A14; A25; A96; D21
Int Pat Class: A61K-007/06; A61K-007/11; C08F-004/00; C08F-018/02;
   C08F-020/00; C08F-220-18; C08F-263/02; C08F-265/06; C08F-265/10;
   C08F-293/00; C08F-297/00; C08G-081/02; C08K-005/04
Number of Patents: 007
Number of Countries: 027
Number of Cited Patents: 016
Number of Cited Literature References: 000
Number of Citing Patents: 000
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(11) EP 1 043 346 B1

(12)

FASCICULE DE BREVET EUROPEEN

(45) Date de publication et mention de la délivrance du brevet: 05.03.2003 Bulletin 2003/10

(51) Int CI.7: **C08F 293/00**, C08G 81/02, A61K 7/06

- (21) Numéro de dépôt: 00400651.6
- (22) Date de dépôt: 09.03.2000
- (54) Composition cosmétique comprenant des polymères ayant une structure en étoiles et leur utilisation notamment en capillaire

Kosmetische Zusammensetzungen aus sternförmigen Polymeren und ihre Anwendung insbesondere für Haare

Cosmetic compositions containing star shaped polymers and their use in particular for hair

- (84) Etats contractants désignés:
 AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
 MC NL PT SE
- (30) Priorité: 06.04.1999 FR 9904258
- (43) Date de publication de la demande: 11.10.2000 Bulletin 2000/41
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- (56) Documents cités:

WO-A-86/00626 DE-A- 19 602 540 US-A- 5 804 664 DE-A- 4 328 004 US-A- 3 907 984

P 1 043 346 B1

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atomes d carbon ; un radical aryl ; un radical hétérocyclyle; étant donné que R²⁰ et R²¹ peuvent être joints de manière à former un cycle, saturé ou insaturé; étant donné que chaque radical peut en outre être substitué avec un radical alkyle ayant 1-6 atomes de carbone, un radical alcoxy ayant 1-6 atomes de carbone ou un radical aryle;

(ii) le monoxyde de carbone; les porphyrines et les porphycènes, éventuellement substitués; l'éthylènediamine et le propylènediamine, éventuellement substitués; les multiamines avec amines tertiaires telles que le pentaméthyldiéthylènetriamine; les aminoalcools tels que l'aminoéthanol et l'aminoprpoanol, éventuellement substitués; les glycols tels que l'éthylèneglycol ou le propylèneglycol, éventuellement substitués; les arènes tels que le benzène, éventuellement substitués; le cyclopentadiène, éventuellement substitué; les pyridines et bipyridines, éventuellement substitué; les cryptands et les éthers-couronnes; la spartéine

- 6. Composition selon l'une des revendications précédentes, dans laquelle l'agent propulseur est choisi parmi, seul ou en mélange, les hydrocarbures volatils tels que le n-butane, le propane, l'isobutane, le pentane, un hydrocarbure chloré et/ou fluoré; le gaz carbonique, le protoxyde d'azote, le diméthyléther (DME), l'azote, l'air comprimé.
- Composition selon l'une des revendications précédentes, dans laquelle l'agent auxiliaire de filmification est choisi parmi, seul ou en mélange :
 - les glycols et leurs dérivés tels que le diéthylène glycol éthyléther, le diéthylène glycol méthyléther, le diéthylène glycol butyléther, le diéthylène glycol hexyléther, l'éthylène glycol butyléther, l'éthylène glycol hexyléther;
 - les esters de glycérol, tels que le diacétate de glycérol et le triacétate de glycérol;
 - les dérivés de propylène glycol et en particulier le propylène glycol phényléther, le propylène glycol diacétate, le propylène glycol méthyléther, le propylène glycol éthyléther, le propylène glycol butyléther, le dipropylène glycol méthyléther, le dipropylène glycol butyléther, le dipropylène glycol éthyléther, le tripropylène glycol butyléther, le tripropylène glycol méthyléther:
 - des esters d'acid s notamment carboxyliques, tels qu des citrates, des phtalat s, des adipa-

- tes, des carbonates, des tartrates, des phosphates, des sébaçates,
- des dérivés oxyéthylénés tels que les huiles oxyéthylénées, notamment les huiles végétales telles que l'huile de ricin; les huiles de silicon oxyéthylénées.
- 8. Composition selon l'une des revendications précédentes, dans laquelle le polymère de structure 'en étoiles' est présent en une quantité comprise entre 1-95% en poids de matière sèche, par rapport au poids total de la composition, de préférence entre 1-50% en poids et préférentiellement entre 1-20% en poids.
- 9. Composition selon l'une des revendications précédentes, dans laquelle le polymère de structure 'en étoiles' est présent dans le milieu sous forme dissoute ou en dispersion, dans une phase aqueuse, organique ou hydroorganique notamment alcoolique ou hydroalcoolique.
- 10. Composition selon l'une des revendications précédentes, se présentant sous la forme d'un spray, d'une laque, d'une mousse, de crème, de gel, d'émulsion, de lotion ou de cire.
- 11. Procédé de maintien ou de mise en forme des cheveux, caractérisé par le fait qu'il consiste à appliquer sur ceux-ci une composition cosmétique selon l'une des revendications précédentes.
- 12. Utilisation d'une composition cosmétique selon l'une des revendications 1 à 10, pour la fabrication d'un produit cosmétique capillaire destiné à maintenir et/ou fixer et/ou traiter la coiffure et/ou les cheveux
- 13. Utilisation selon la revendication 12, pour la fabrication d'un produit de coiffage tel qu'une laque, un spray ou une mousse, en vue d'obtenir le maintien ou la mise en forme de la coiffure.

45 Claims

Hair cosmetic composition, in particular for the treatment and/or the fixing of the hair, comprising, in a cosmetically acceptable medium comprising at least one constituent chosen from water; one or more cosmetically acceptable solvents, such as alcohols comprising 1 to 4 carbon atoms, ethers, ketones or C₁-C₃ lower carboxylic acid esters; cosmetic active principles; softeners; antioxidants; opacifiers; antifoaming agents; preservatives; sequestering agents; UV screening agents; ceramides; antidandruff agents; complexing agents; agents for dramatic hair loss; antifungal or antisep-

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tic agents; thickeners; fixing or nonfixing polymers; conditioners; propellants; basifying or acidifying agents; hydrophilic polymers; film-forming polymers, in particular in aqueous dispersion; surfactants, in particular anionic or nonionic surfactants, optionally comprising silicone groups; or an additional agent which is able to form a film, such as a plasticizing agent and/or a coalescence agent; at least one polymer with a "star" structure capable of being obtained by atom transfer radical polymerization.

- of one or more radically polymerizable monomers, chosen from:
 - (i) acrylic or methacrylic esters obtained from linear, branched or cyclic aliphatic alcohols and/or from aromatic alcohols comprising 1 to 20 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate or tert-butyl (meth)acrylate;
 - (ii) C₁-C₄ hydroxyalkyl (meth)acrylates, such as 2-hydroxyethyl (meth)acrylate, or 2-hydroxypropyl (meth)acrylate:
 - (iii) ethylene glycol, diethylene glycol or polyethylene glycol (meth)acrylates with a hydroxyl or ether end;
 - (iv) vinyl, allyl or methallyl esters obtained from linear or branched C₁-C₁₀ or cyclic C₁-C₆ aliphatic alcohols and/or from C₁-C₆ aromatic alcohols, such as vinyl acetate, vinyl propionate, vinyl benzoate or vinyl tert-butylbenzoate;
 - (v) N-vinylpyrrolidone; vinylcaprolactam; vinyl-N-alkylpyrroles having 1 to 6 carbon atoms; vinyloxazoles; vinylthiazoles; vinylpyrimidines; vinylimidazoles; or vinyl ketones;
 - (vi) (meth)acrylamides obtained from linear, branched or cyclic aliphatic amines and/ or from aromatic amines comprising 1 to 20 carbon atoms, such as tert-butylacrylamide; or (meth)acrylamides, such as acrylamide, methacrylamide or di(C₁-C₄)alkyl (meth)acrylamides;
 - (vii) olefins, such as ethylene, propylene, styrene or substituted styrene;
 - (viii) fluorinated or perfluorinated acrylic or vinyl monomers, in particular (meth)acrylic esters with perfluoroalkyl units;
 - (ix) monomers comprising an amine functional group in the free or else partially or completely neutralized or else partially or completely quaternized form, such as dimethylaminoethyl (meth)acrylate, dimethylaminoethylmethacrylamide, vinyl

amine, vinylpyridine or diallyldimethylammonium chloride;

(x) carboxybetaines or sulphobetaines obtained by partial or complete quaternization of monomers comprising thylenic unsaturation comprising an amine functional group by sodium salts of carboxylic acids comprising a mobile halide (sodium chloroacetate, for example) or by cyclic sulphones (propane sulphone);

(xi) silicone-comprising (meth)acrylates or (meth)acrylamides, in particular (meth) acrylic esters comprising siloxane units; (xii) their mixtures;

in the presence

- of an initiator having at least two atoms and/or groups radically transferable by polymerization,
- of a compound comprising a transition metal, capable of participating in a reduction stage with the initiator and a "dormant" polymer chain, chosen from those of formula Mⁿ⁺X'_n, in which:
 - M is chosen from Cu, Au, Ag, Hg, Ni, Pd, Pt, Rh, Co, Ir, Fe, Ru, Os, Re, Mn, Cr, Mo, W, V, Nb, Ta and Zn, and
 - X' represents a halogen (in particular bromine or chlorine), OH, (O)_{1/2}, an alkoxy radical having 1-6 carbon atoms, (SO₄)_{1/2}, (PO₄)_{1/3}, (HPO₄)_{1/2}, (H₂PO₄) and a triflate, hexafluorophosphate, methanesulphonate, arylsulphonate, SeR, CN, NC, SCN, CNS, OCN, CNO, N₃ and R'CO₂, in which R represents an aryl or linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms and R' represents H or a linear or branched alkyl radical having 1-6 carbon atoms or an aryl radical which is optionally substituted by one or more halogen atoms, in particular fluorine and/or chlorine atoms;
- n is the charge on the metal;

and

- of a ligand chosen from:

(i) compounds comprising at least one nitrogen (N), oxygen (O) phosphorus (P) and/or sulphur (S) atom which are capable of coordinating via a σ bond to the said compound comprising a transition metal; (ii) compounds comprising at least two carbon atoms capable of coordinating via a π

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bond to the said compound comprising a transition metal:

(iii) compounds comprising at least on carbon atom capable of coordinating via a σ bond to the said compound comprising a transition metal but which do not form a carbon-carbon bond with the monomer during the polymerization;

(iv) compounds capable of coordinating via a μ or η bond to the said compound comprising a transition metal;

the said polymer comprising one or more monomers Mi, the corresponding homopolymer of which exhibits a Tg of greater than or equal to 10°C, preferably greater than or equal to 15°C and even better still of greater than or equal to 20°C; this or these monomers Mi being present, in the final polymer, in an amount of between 55 and 95% by weight, preferably in an amount of 60 to 93% by weight and even better still in an amount of 65 to 90% by weight, with respect to the total weight of monomers; and the said polymer furthermore comprising one or more monomers Mj, the corresponding homopolymer of which exhibits a Tg of less than or equal to 10°C, preferably of less than or equal to 5°C and even better still of less than or equal to 0°C; this or these monomers Mj being present, in the final polymer, in an amount of between 5 and 45% by weight, preferably in an amount of 7 to 40% by weight and even better still in an amount of 10-35% by weight, with respect to the total weight of mono-

- Composition according to the preceding claim, in 35 which the monomers are chosen from:
 - (meth)acrylic esters obtained from linear or branched aliphatic alcohols, preferably C₁-C₂₀ alcohols:
 - C₁-C₂₀ (meth)acrylic esters comprising perfluoroalkyl units;
 - C₁-C₂₀ (meth)acrylic esters comprising siloxane units;
 - (meth)acrylamides obtained from linear, branched or cyclic aliphatic amines and/or from aromatic amines preferably comprising 1 to 20 carbon atoms, such as tert-butylacrylamide; or (meth)acrylamides, such as acrylamide, methacrylamide or di(C₁-C₄)alkyl(meth)acrylamides;
 - vinyl, allyl or methallyl esters obtained from linear or branched C₁-C₁₀ or cyclic C₁-C₆ aliphatic alcohols:
 - vinylcaprolactam;
 - optionally substituted styrene;
 - their mixtures.

- Composition according to one of the preceding claims, in which the initiator is chosen from the compounds of formula:
 - R¹¹_xR¹²_yR¹³_zC-(RX)_t, in which x, y and z represent an int ger ranging from 0 to 4, t an integer ranging from 1 to 4, and x+y+z = 4-t;
 - R13_xC₆-(RX)_y (saturated ring with 6 carbons), in which x represents an integer ranging from 7 to 11, y represents an integer ranging from 1 to 5, and x+y = 12;
 - R13_xC₆-(RX)_y (unsaturated ring with 6 carbons), in which x represents an integer ranging from 0 to 5, y represents an integer ranging from 1 to 6, and x+y = 6;
 - -[-(R¹¹)(R¹²)(R¹³)C-(RX)-]_n, in which n is greater than or equal to 1; cyclic or linear;
 - -[-(R¹²)_xC₆(Rx)_y-R¹¹-]_n, in which x represents an integer ranging from 0 to 6, y represents an integer ranging from 1 to 6 and n is greater than or equal to 1, with x+y = 4 or 6; cyclic or linear;
 - -[-(R¹²)_xC₆(RX)_y-R¹¹-]_n, in which x represents an integer ranging from 0 to 12, y represents an integer ranging from 1 to 12 and n is greater than or equal to 1, with x+y = 10 or 12; cyclic or linear.
 - [OSi(R¹¹)_x(RX)_y]_n, cyclic or linear, in which x and y represent an integer ranging from 0 to 2 and n is greater than or equal to 1, with x+y = 2;
 - R11N-X2
 - (R¹¹)_xP(O)_y-X_{3-x}, in which x and y represent integers ranging from 0 to 2 and x+y = 5;
 - (R¹¹O)_xP(O)_y-X_{3-x}, in which x and y represent integers ranging from 0 to 2 and x+y = 5;
 - -[(R¹¹)_tN_zP(O)_x(O-RX)_y-]_n, cyclic or linear, in which x represents an integer ranging from 0 to 4, y represents an integer ranging from 1 to 5, z represents an integer ranging from 0 to 2, t represents an integer ranging from 0 to 3 and n is greater than or equal to 1;

in which:

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- R R¹¹, R¹² and R¹³ represent, independently of one another, a hydrogen or halogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10 and more preferably 1-6 carbon atoms; a cycloalkyl radical having 3-8 carbon atoms; a -C(=Y)R⁵, -C(=Y)NR⁶R⁷ or -R⁸₃Si radical; -COCI; -OH; -CN; an alkenyl or alkynyl radical having 2-20, preferably 2-6, carbon atoms; an oxiranyl or glycidyl radical or an alkylene or alkenylene radical substituted with an oxiranyl or a glycidyl; an aryl, heterocyclyl, aralkyl or aralkenyl radical; or an alkyl radical having 1-6 carbon atoms in which all or part of the hydrogen atoms are substituted either by halogen atoms, such as fluorine, chlorine or

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bromine, or by an alkoxy group having 1-4 carbon atoms or by an aryl, heterocyclyl, -C(=Y) R⁵, -C(=Y)NR⁶R⁷, oxiranyl or glycidyl radical;

- X represents a halogen atom, such as Cl, Br or I, or an -OR', -SR, -SeR, -OC(=O)R', -OP(=O) R', -OP(=O) (OR')₂, -OP(=O)OR', -O-NR'₂, -S-C (=S)NR'₂, -CN, -NC, -SCN, -CNS, -OCN, -CNO or -N₃ radical, in which R' represents an alkyl radical having 1-20 carbon atoms which is optionally substituted by one or more halogen atoms, in particular fluorine and/or chlorine atoms, and R represents a linear or branched alkyl or aryl radical having 1-20, preferably 1-10, carbon atoms, it additionally being possible for the -NR'₂ group to represent a cyclic group, the two R' groups being joined so as to form a 5-, 6- or 7-membered heterocycle;
- Y represents O, S or NR⁸ (preferably O);
- R⁵ represents a linear or branched alkyl, alkylthio or alkoxy radical having 1-20 carbon atoms; an OH radical; an OM' radical with M' = alkali metal; an aryloxy radical or a heterocyclyloxy radical;
- R⁶ and R⁷ represent, independently of one another, H or a linear or branched alkyl radical having 1-20 carbon atoms; it being given that R⁶ and R⁷ can be joined to form an alkylene group having 2-7, preferably 2-5, carbon atoms;
- R8 represents H; a linear or branched alkyl radical having 1-20 carbon atoms or an aryl radical.
- 4. Composition according to one of the preceding claims, in which the initiator is chosen from:
 - octa(2-isobutyrylbromide)-octa (tert-butyl)calix (8)arene,
 - octa(2-propionylbromide)-octa(tert-butyl)calix
 (8)arene, and
 - hexakis(α-bromomethyl)benzene.
- Composition according to one of the preceding claims, in which the ligand is chosen from:
 - (i) the compounds of formula: R^9 -Z- $(R^{14}$ -Z)_m- R^{10} or $R^{20}R^{21}C[C(=Y)R^5]$ in which:
 - R⁹ and R¹⁰ are, independently of one another, a hydrogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms; an aryl radical; a heterocyclyl radical; or an alkyl radical having 1-6 carbon atoms which is substituted with an alkoxy radical having 1-6 carbon atoms or a dialkylamino radical having 1-4 carbon atoms or a -C(=Y)R⁵ or -C(=Y) NR⁶R⁷ and/or YC(=Y)R⁸ radical, R⁵ to R⁸

- and Y having the definitions given in Claim 3; it being given that R⁹ and R¹⁰ can be join d so as to form a saturated or unsaturated ring:
- R14 represents, independently of one another, a divalent group chosen from alkanediyls having 2-4 carbon atoms; alkenediyls having 2-4 carbon atoms; cycloalkanediyls having 3-8 carbon atoms; cycloalkenediyls having 3-8 carbon atoms; arenediyls and heterocyclylenes;
- Z represents O, S, NR¹⁵ or PR¹⁵, with R¹⁵ representing H; a linear or branched alkyl radical having 1-20 carbon atoms; an aryl radical; a heterocyclyl radical; or an alkyl radical having 1-6 carbon atoms which is substituted with an alkoxy radical having 1-6 carbon atoms or a dialkylamino radical having 1-4 carbon atoms or a -C(=Y)R⁵ or -C(=Y)NR⁶R⁷ and/or YC(=Y)R⁸ radical (R⁵ to R⁸ and Y having the definitions given in Claim 3;
- m is between 0 and 6;
- R²⁰ and R²¹ are, independently of one another, a hydrogen atom; a halogen atom; a linear or branched alkyl radical having 1-20, preferably 1-10, carbon atoms; an aryl radical; or a heterocyclyl radical; it being given that R²⁰ and R²¹ can be joined so as to form a saturated or unsaturated ring; it being given that, in addition, each radical can be substituted with an alkyl radical having 1-6 carbon atoms, an alkoxy radical having 1-6 carbon atoms or an aryl radical;
- (ii) carbon monoxide; optionally substituted porphyrins and porphycenes; optionally substituted ethylenediamine and propylenediamine; polyamines with tertiary amines, such as pentamethyldiethylenetriamine; aminoalcohols, such as aminoethanol and aminopropanol, which are optionally substituted; glycols, such as ethylene glycol or propylene glycol, which are optionally substituted; arenes, such as benzene, which are optionally substituted; optionally substituted cyclopentadiene; optionally substituted pyridines and bipyridines; acetonitrile; 1,10-phenanthroline; cryptands and crown ethers; or sparteine.
- 6. Composition according to one of the preceding claims, in which the propellant is chosen from, alone or as a mixture, volatile hydrocarbons, such as nbutane, propane, isobutane, pentane or a chlorinated and/or fluorinated hydrocarbon; carbon dioxide gas, nitrous oxide, dimethyl ether (DME), nitrogen or compressed air.

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- Composition according to one of the preceding claims, in which the additional agent which is abl to form a film is chosen from, alone or as a mixtur:
 - glycols and their derivatives, such as diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol butyl ether, diethylene glycol hexyl ether, ethylene glycol butyl ether or ethylene glycol hexyl ether;
 - glycerol esters, such as glyceryl diacetate and glyceryl triacetate;
 - propylene glycol derivatives and in particular propylene glycol phenyl ether, propylene glycol diacetate, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol butyl ether, dipropylene glycol methyl ether, dipropylene glycol butyl ether, dipropylene glycol ethyl ether, tripropylene glycol butyl ether or tripropylene glycol methyl ether;
 - acid esters, in particular carboxylic acid esters, such as citrates, phthalates, adipates, carbonates, tartrates, phosphates or sebacates,
 - oxyethylenated derivatives, such as oxyethylenated oils, in particular vegetable oils, such as caster oil; or oxyethylenated silicone oils.
- 8. Composition according to one of the preceding claims, in which the polymer with the "star" structure is present in an amount of between 1-95% by weight on a dry basis, with respect to the total weight of the composition, preferably between 1-50% by weight and preferentially between 1-20% by weight.
- Composition according to one of the preceding claims, in which the polymer with the "star" structure is present in the medium in the form dissolved or in dispersion in an aqueous, organic or aqueous/organic phase, in particular an alcoholic or aqueous/ alcoholic phase.
- Composition according to one of the preceding claims, which is provided in the form of a spray, lacquer, foam, cream, gel, emulsion, lotion or wax.
- Process for the form retention or shaping of the hair, characterized in that it consists in applying, to the latter, a cosmetic composition according to one of the preceding claims.
- 12. Use of a cosmetic composition according to one of Claims 1 to 10 in the manufacture of a hair cosmetic product intended to retain the form of and/or fix and/ or treat the hairstyle and/or the hair.
- 13. Use according to Claim 12 in the manufacture of a styling product, such as a lacquer, a spray or a foam, for the purpose of obtaining form retention or

shaping of th hairstyle.

Patentansprüch

- Kosmetische Zusammensetzung für das Haar, insbesondere zur Behandlung und/oder Fixierung der Haare, die in einem kosmetisch akzeptablen Medium mindestens einen Bestandteil, der unter den folgenden Verbindungen ausgewählt ist: Wasser; einem oder mehreren kosmetisch akzeptablen Lösungsmitteln, wie C₁₋₄-Alkoholen, Ethern, Ketonen, Estern von niederen Carbonsäuren mit 1 bis 3 Kohlenstoffatomen; kosmetischen Wirkstoffen; reizlindernden Wirkstoffen, Antioxidantien, Trübungsmitteln, Schaumverhütungsmitteln, Konservierungsmitteln, Maskierungsmitteln, UV-Filtern, Ceramiden; Antischuppenmitteln; Komplexbildnern; Wirkstoffen gegen Haarausfall; antimykotischen oder antiseptischen Wirkstoffen; Verdickungsmitteln, fixierenden oder nichtfixierenden Polymeren oder Konditioniermitteln; Treibmitteln, Alkalisierungsmitteln oder Ansäuerungsmitteln; hydrophilen Polymeren; filmbildenden Polymeren, insbesondere in wässriger Dispersion; grenzflächenaktiven Stoffen und insbesondere anionischen oder nichtionischen grenzflächenaktiven Stoffen, die ggf. siliconhaltig sind; Hilfsmitteln zur Filmbildung wie Weichmachem und/oder Koaleszenzmitteln; und mindestens ein Polymer mit "sternförmiger" Struktur enthält, das erhältlich ist durch radikalische Atomtransferpolymerisation:
 - eines oder mehrerer radikalisch polymerisierbarer Monomere, die ausgewählt sind unter:
 - (i) den Acrylestern oder Methacrylestern, die ausgehend von aliphatischen, geradkettigen, verzweigten, cyclischen und/oder aromatischen Alkoholen vorzugsweise mit 1 bis 20 Kohlenstoffatomen hergestellt werden, wie beispielsweise Methyl(meth) acrylat, Ethyl(meth)-acrylat, Propyl(meth) acrylat, Butyl(meth)acrylat, Isobutyl(meth) acrylat und t-Butyl(meth)acrylat;
 - (ii) C₁₋₄-Hydroxyalkyl(meth)acrylaten, wie 2-Hydroxyethyl(meth)acrylat oder 2-Hydroxypropyl(meth)acrylat;
 - (iii) Ethylenglykol(meth)acrylaten, Diethylenglykol(meth)acrylaten und Polyethylenglykol(meth)-acrylaten mit endständigen Hydroxy- oder Ethergruppen;
 - (iv) Vinylestern, Allylestern oder Methallylestern, die ausgehend von aliphatischen, geradkettigen oder verzweigten C₁₋₁₀-Al-